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Publication date:
2014

Document Version
Peer reviewed version

Defect-Oxygen assisted direct write technique for nanopatterning graphene

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Abstract

In recent years, nanopatterned graphene has been attracting considerable attention due to the possibility of tuning the graphene electronic properties in many different ways through controlled patterning. It has been theoretically predicted that by properly shaping the nanopattern, graphene can display several new interesting properties such as a magnetic dipole or a strong anisotropy in the transport regime [1][2]. One of the most important modifications that can be created by nanopatterning is a band gap in the density of states of graphene by cutting graphene into nanoribbons [3] or creating an antidot lattice [4]. For all these applications the nanopattern features has to be 20 nm and below, which imposes stringent requirements for the resolution of the patterning techniques to be used. So far, the most used nanopatterning techniques which can achieve critical dimensions below 20nm in graphene are e-beam lithography and block copolymer lithography [3][5]. The main common issue with these techniques is that they require graphene to be in contact with a polymer, which inevitably alters the properties of graphene. One of the most used polymer to achieve under 20nm features in e-beam lithography is HSQ [3], which is known for doping graphene and it is very hard to remove [3][6]. PMMA is also used, but it presents similar problems of unwanted residues difficult to fully remove [7]. On the other hand Block copolymer process often involves the deposition of a SiO_2 layer on top of graphene creating defects in the graphene lattice [5]. Thiele et al. recently demonstrated the possibility of etching graphene without any mask. They etched graphene with an e-beam combined with an oxygen rich atmosphere using an environmental SEM [9]. Unfortunately E-SEMs are not widely available and are costly. Here, we present a new nanopatterning technique that does not require any polymer and also does not require an environmental SEM, but only an EBL system and an oven that operates in air at atmospheric pressure. In Figure 1a the positive two-step direct write nanopatterning process is illustrated. The EBL system was used to irradiate the samples, writing the patterns that had to be etched into graphene. The e-beam irradiation is used to selectively damage the graphene crystal lattice in the exposed areas. In order to quantify the defect density induced by the irradiation Raman spectroscopy was used and in Figure 1b the ratio I(D)/I(G) is reported as a function of the irradiation dose. As expected the I(D)/I(G) ratio is increasing starting from the lowest dose (0.185 C/cm^2) till 0.7 C/cm^2, indicating that the defect density increases with the dose. For doses larger than 0.7 C/cm^2 till ~3 C/cm^2 the ratio decreases due to the high density of defects that destroys the hexagonal carbon rings (characteristic length between defects is approximately few nanometers). In this range the nanocrystalline structure is turned into an amorphous structure with increasing sp^3 content. For higher doses the ratio is influenced by the e-beam induced deposition of amorphous carbon on the irradiated areas and it does not decrease. Figure 2a shows one of the samples after direct write, where 4x4 μm squares have been written with different doses. The Figure 2b presents a Raman Map of the I(D)/I(G) ratio, showing how the damage is localized in the squares. Figure 2c presents the optical images of the etching sequence of this sample etched in air at 435 ^oC. After 16 minutes the etching is completed for the three different doses as shown in Figure 2d where the map of the 2D peak intensity is reduced over 10 times inside the squares. Figure 3a presents the SEM images of two squares written with 5 C/cm^2 and 10 C/Cm^2 as the etching proceed. The graph in Figure 3b shows the remaining graphene in the written areas after 12 minutes of etching as a function of the dose. It is evident how a larger dose leads to faster etch rate. This novel nanopatterning technique has been employed to pattern nanoholes with a diameter of 40 nm and lines down to 40 nm in width (see Figure 4).

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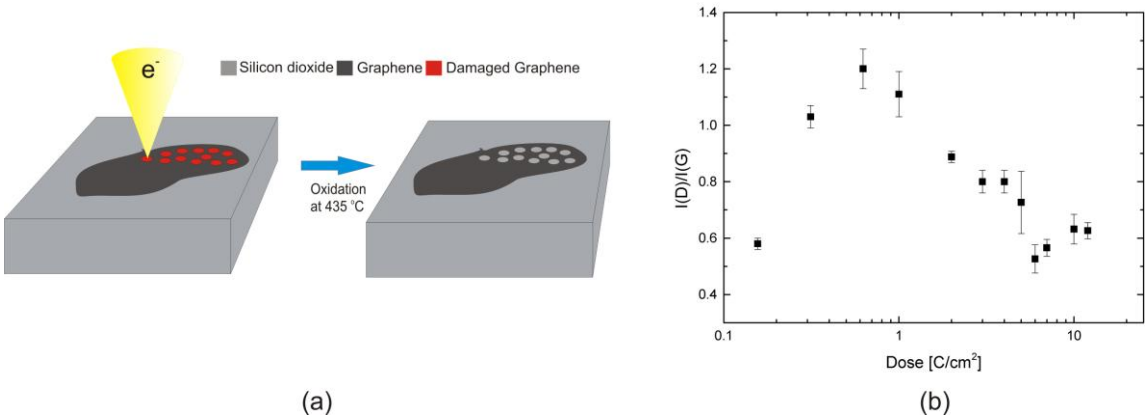

Figure 1. (a) Illustration of the direct write nanopatterning method. (b) I(D)/I(G) as a function of the dose use after the direct write.

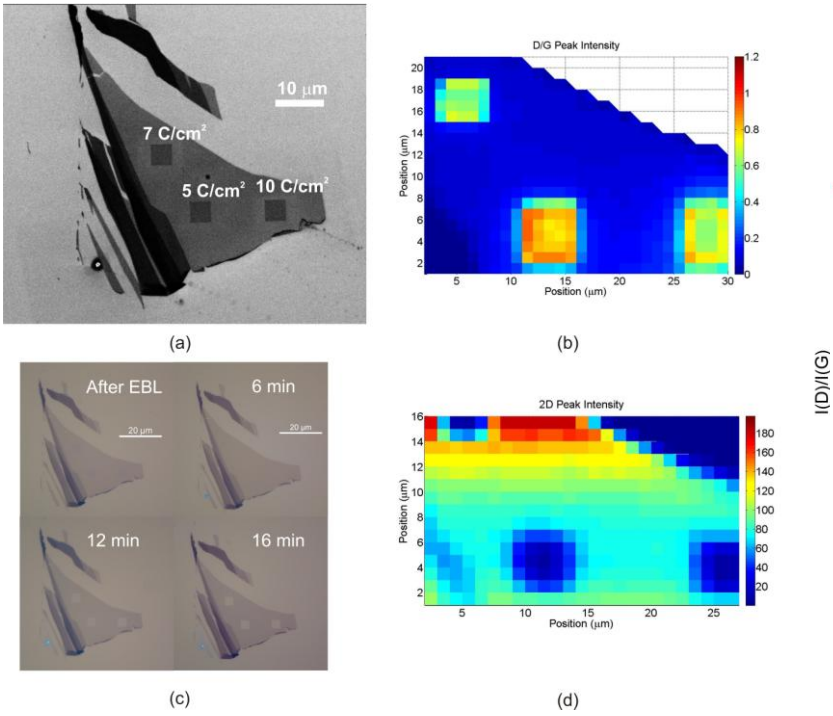

Figure 2. (a) SEM image of one of the sample after direct write. (b) I(D)/I(G) Raman map of the sample. (c) Optical images illustrating the etching sequence of the sample. (d) I(2D) Raman map after etching for 16 minutes.

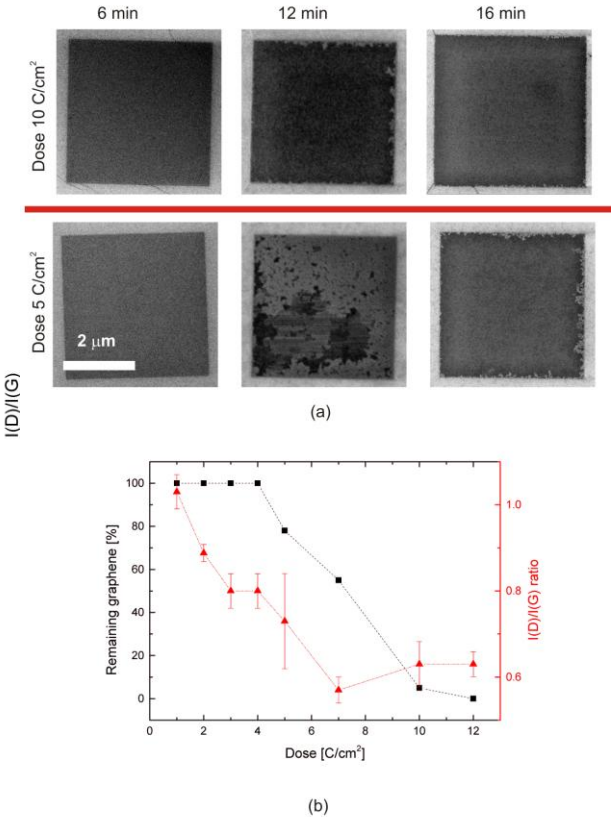

Figure 3. (a) SEM images illustrating the etching sequence for different two doses. (b) The percentage of remaining graphene after 12 minutes of etching is plot as a function of the dose. The I(D)/I(G) ratio is also reported

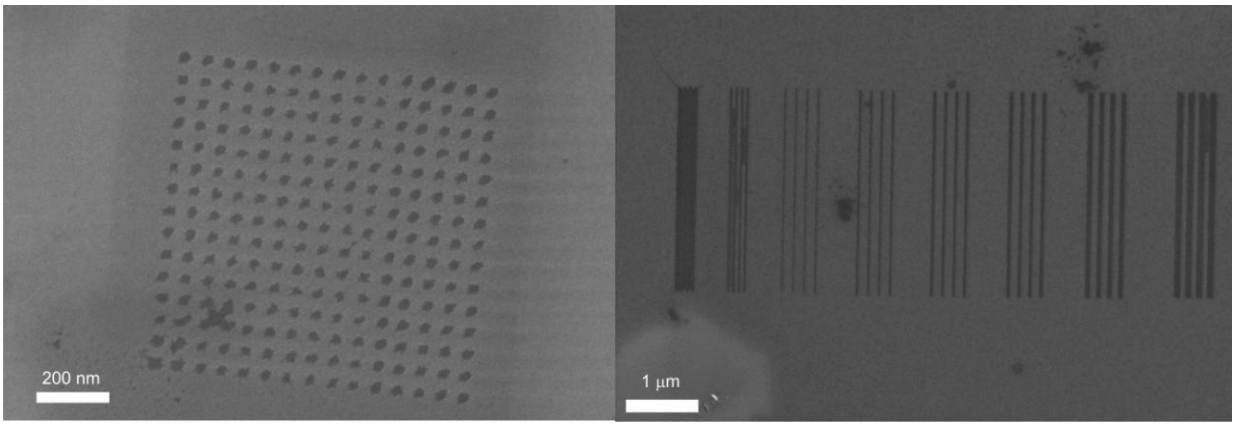

Figure 4. Nanoholes in a square pattern with 40 nm diameter and lines down to 40 nm in width etched into graphene.